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3,361,564

## AMINE BORANE AS FOGGING AGENT IN DIRECT POSITIVE

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This invention relates to radiation-sensitive photographic materials, and more particularly to radiation-sensitive silver halide developing-out emulsions, and elements coated with such emulsions. Still more particularly, this invention relates to radiation-sensitive silver halide developing emulsions of the direct positive type. This invention, in addition, relates to processes for producing direct positive images utilizing the above emulsions.

Developing-out photographic emulsions are classified broadly into two types, namely (1) those which, when exposed and developed produce negative images of the originals and (2) those which when exposed and developed, produce positive images of the originals. This invention is concerned with this latter type.

Direct positive photographic elements have long been known and are highly useful in the copying and graphic arts fields for duplicating work.

Direct positive images may be produced in a variety of ways using silver halide emulsions. For example, a silver halide emulsion may be given a short over-all exposure of high intensity radiation and then given a longer image-wise exposure to radiation of lower intensity. Upon development, a direct positive image will be obtained. Another method is to expose imagewise and develop and then flash expose and redevelop. A still further method is to chemically fog the silver halide grains with, for example, formaldehyde, hydrazine, sodium arsenate, silver ions and other non sulfide fogging agents, instead of using a solarizing exposure. Upon imagewise exposure and development of such a chemically fogged element, a positive image is obtained. In direct positive photographic elements utilizing this latter method, there is usually incorporated a desensitizing compound, usually a colored desensitizing dye.

All of the above methods and elements leave something to be desired and suffer from such shortcomings as low reversal density, impractically long exposure times, undesirable stain from desensitizing dyes as well as undesirable contrast. Using more than one exposure or development step adds to the number of operations and to the complexity of the process. The use of formaldehyde as a chemical fogging agent is undesirable because it has a strong effect on the hardness of the gelatin colloid carrier.

It is an object of this invention to provide new and useful direct positive emulsions containing novel chemical fogging agents. It is a further object of this invention to provide direct positive photographic elements having exposure requirements equal to those required by ordinary contact, silver halide emulsion coated papers. A still further object is to provide direct positive photographic elements which eliminate the need for multiple exposure steps, multiple developing steps or the presence of desensitizing compounds for the production of direct positive images. A still further object is to provide a process of producing direct positive images having clean whites, and good sensitometric characteristics. Other objects will appear hereinafter.

These and other objects are accomplished according to this invention by incorporating an amine borane compound as a chemical fogging agent in a silver halide emulsion. The emulsion preferably is a gelatino-silver chloride emulsion containing from about 80 to 90% by

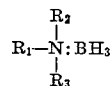
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weight of silver bromide and optionally may contain, in addition to the two halides, from 0 to 6% by weight of silver iodide.

The borane fogging agents may be added to the emulsions in amounts ranging from 0.00033 gram to 12.0 grams per mole of silver halide and preferably from 0.013 to 1.3 grams per mole of silver halide. They may be added either as a solid or dissolved in a suitable solvent. The effectiveness of the borane compounds in fogging a silver halide emulsion is influenced by the pH of the system, the higher the pH, the greater the fogging for a given amount of borane compound. Of course, certain of the borane compounds are more effective than others when used in equivalent quantities. The fogging amounts of a particular amine borane within the above limits can easily be determined empirically. The fogging effect produced by the borane compounds is bleachable by light exposure prior to development. The maximum amount of amine borane should be limited to create no more fog than that which can be bleached by light exposure prior to development. A suitable developer may be any conventional alkaline photographic developing solution which would be used for standard processing of the above direct positive emulsions in the absence of the amine borane compounds. Although the mechanism is not clearly understood, the light bleaching effect is believed due to solarization. While the amine borane compounds will act to chemically fog all types of emulsions, the solarizing effect appears to be more efficient in silver chlorobromide emulsions.

Among the amine borane compounds which have been found useful as chemical fogging compounds in this invention are the following:

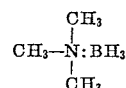
A. Alkyl amine-boranes: Typical of these amine boranes are those of the formula



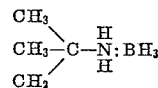
where  $R_1$  is an alkyl radical of about 1 to 20 carbon atoms and  $R_2$  and  $R_3$  are the same as  $R_1$  or hydrogen.

Examples of such boranes are:

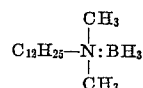
(1) Trimethylamine borane,



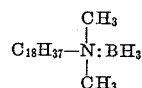
(2) Tertiary butyl amine borane,



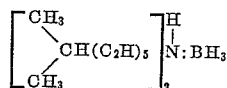
(3) Dimethyl dodecyl amine borane,



(4) Dimethyl octadecyl amine borane,

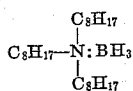


(5) Di-isooctyl amine borane,



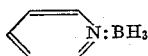
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(6) Alamine (tricaprylamine) borane,

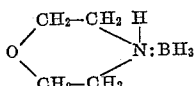


B. Heterocyclic amine boranes such as:

(1) Pyridine borane,

(2) Picoline borane and isomeric mixtures of the three isomers of picoline borane (i.e.,  $\alpha$ ,  $\beta$ , and  $\gamma$  picoline borane),

(3) Morpholine borane,



For most efficient fogging action it is preferred that the chemical fogging agents of this invention be added to the silver halide emulsion after it has been made, ripened, and washed to remove the excess soluble salts resulting from the precipitation of the silver halides. Conveniently, the borane compounds are added just prior to or during the digestion or after-ripening period. The pH of the emulsion is adjusted to between 5 and 9 and preferably to 8.0-8.5 and maintained at this level during digestion. After digestion the pH is lowered to between 5 and 6, and the conventional coating aids are added. Coating aids such as saponin, sodium salts of polyether sulfonates, alkyl sulfonates, cetyl betaine, etc. can be utilized. The emulsion is then coated and dried in the manner known to those skilled in photographic manufacturing methods.

The sensitometric characteristics of the direct positive emulsions may be determined by processing test strips of the coated layers in the following manner. A test strip in each of the following examples is fixed out in a conventional photographic fixer to provide a means of establishing the minimum density ( $D_{\min.}$ ). Test strips are exposed in an intensity scale sensitometer (described on page 616, Mees, *The Theory of the Photographic Process*, MacMillan Company, New York, 1942) using a  $\sqrt{2}$  step wedge and 20 Luxometer units of exposure. The exposed strip is developed for 1½ minutes at 68° F. in a developer having the composition:

|                              |              |      |
|------------------------------|--------------|------|
| Water                        | -----ml----- | 750  |
| Metol                        | -----gm----- | 1.5  |
| Sodium sulfite (anhydrous)   | -----gm----- | 19.5 |
| Hydroquinone                 | -----gm----- | 6.0  |
| Sodium carbonate (anhydrous) | -----gm----- | 24.0 |
| Potassium bromide            | -----gm----- | 0.8  |
| Water to make 1.0 liter.     |              |      |

The developed strip is then immersed in a conventional short stop for 5 to 10 seconds and then fixed for 3 minutes in a conventional fixer, and then washed and dried.

In evaluation of the processed strips, the minimum density ( $D_{\min.}$ ) equals the lowest density above that of the fixed out strip mentioned above. The maximum density is the highest density above  $D_{\min.}$  Total scale is given in terms of log  $E$  range and is the difference between log  $E$  (exposure) at 0.01 above  $D_{\min.}$  and log  $E$  at 2.5 above  $D_{\min.}$  Where in the following examples  $D_{\max.}$  is below 2.5 total scales are not given. The speed of a typical commercial direct positive in terms of  $100/E \times 10^{-5}$  is 10.3 and the conventional material has a  $D_{\min.}$  of 0.02 and a  $D_{\max.}$  of 3.5 and a total scale of 0.40.

The invention will now be illustrated in and by the following examples:

#### Example I

To an acidified aqueous solution of gelatin containing 1 mol of potassium chloride there was rapidly added 1

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mol of silver nitrate in aqueous solution. To the resulting mixture there was added 0.5 mol of potassium bromide aqueous solution and the emulsion was then ripened by heating for 40 min. at 140° F.

The resulting emulsion was then cooled, washed and redispersed in the manner disclosed in Moede, U.S. Patent 2,772,165, issued Nov. 27, 1956. At this stage 0.04 mol of potassium bromide was added. The temperature of the redispersed emulsion was raised to 130° F. and there was then added 167 grams of gelatin, .30 mole potassium bromide in an aqueous solution, water and 0.13 g. of trimethylamine borane from a 1:1000 aqueous solution. The pH was adjusted to 8.0 to 8.5 with borax and digested at 130° F. for 40 minutes. The pH was reduced to 5.0-5.5 with citric acid and the usual coating aids including a gelatin hardener were added and the emulsion was coated on a 4 mil polyester film support and dried in the conventional manner.

Sensitometric evaluation adduced the following data:

|                             |       |      |
|-----------------------------|-------|------|
| $D_{\min.}$                 | ----- | 0.07 |
| $D_{\max.}$                 | ----- | 3.00 |
| Speed                       | ----- | 245  |
| Total scale (log $E$ range) | ----- | 1.05 |

#### Example II

To an acidified aqueous solution of gelatin containing 1 mol of potassium chloride there was rapidly added 1 mol in aqueous solution of silver nitrate. There was then added 1.6 mol excess of potassium chloride and the emulsion was ripened for 20 minutes at 140° F. After ripening, 1.6 mols of potassium bromide was added and the resulting emulsion was washed and redispersed as described in Example I. To the redispersed emulsion there was added 167 grams of gelatin, water and 0.17 gram of trimethylamine borane (1:1000  $\text{H}_2\text{O}$ ). The usual coating aids including a gelatin hardener were added and the emulsion was coated and dried.

Sensitometric evaluation of the coated emulsion provided the following data:

|             |       |      |
|-------------|-------|------|
| $D_{\min.}$ | ----- | 0.02 |
| $D_{\max.}$ | ----- | 1.75 |
| Speed       | ----- | 690  |
| Total scale | ----- | ---  |

#### Example III

To an HCl acidified aqueous solution of gelatin containing 1 mol of potassium chloride there was slowly added an aqueous solution of 1 mol of silver nitrate. To the mixture there was then added an aqueous solution of 1.6 mol of potassium bromide. The emulsion was then ripened for 40 minutes at 130° F. After ripening, the emulsion was coagulated and washed and redispersed with the addition of 0.04 mol of potassium bromide. The temperature was raised to 130° F. and 84 grams of gelatin, water and 0.13 gram of trimethylamine borane were added. The pH was raised to 8.0 to 8.5 with borax and the emulsion was digested for 40 minutes at 130° F. The pH was reduced to 5.0 to 5.5 with citric acid. The usual coating aids including a gelatin hardener were added and the emulsion coated on a polyester film and dried in the conventional manner. Sensitometric evaluation gave the following data:

|             |       |      |
|-------------|-------|------|
| $D_{\min.}$ | ----- | 0.02 |
| $D_{\max.}$ | ----- | 3.50 |
| Speed       | ----- | 610  |
| Total scale | ----- | 1.06 |

#### Example IV

Example III was repeated using 10.6 grams of alamine (tricaprylamine) borane per mol of silver halide in place of the trimethylamine borane. All other operations and

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processing were the same. Sensitometric evaluation gave the following data:

|                         |      |
|-------------------------|------|
| D <sub>min.</sub> ----- | 0.00 |
| D <sub>max.</sub> ----- | 1.78 |
| Speed-----              | 2700 |
| Scale-----              |      |

*Example V*

Example III was repeated except that 0.67 gm. of diisooctyl amine borane per mole of silver halide were used in place of trimethyl amine borane. Sensitometric data were as follows:

|                         |      |
|-------------------------|------|
| D <sub>min.</sub> ----- | 0.01 |
| D <sub>max.</sub> ----- | 0.93 |
| Speed-----              |      |
| Scale-----              |      |

*Example VI*

Example III was repeated except that three samples were made containing 0.67 gram, 1.3 gram and 4.0 grams of dimethyloctadecylamine borane per mole of silver halide instead of the trimethyl amine borane. Sensitometric evaluation provided the following data:

|               | D <sub>min.</sub> | D <sub>max.</sub> | Speed          | Total Scale |
|---------------|-------------------|-------------------|----------------|-------------|
| 0.67 gm.----- | 0.01              | 1.45              |                |             |
| 1.30 gm.----- | 0.00              | 2.31              |                |             |
| 4.00 gm.----- | 0.08              | 2.74              | 2,920<br>1,401 | 1.7         |

*Example VII*

Example III was repeated except that three samples were made containing 0.67 gram, 1.3 grams, and 4.0 grams of dimethyldodecylamine borane per mole of silver halide instead of trimethylamine borane. Sensitometric evaluation provided the following data:

|               | D <sub>min.</sub> | D <sub>max.</sub> | Speed | Total Scale |
|---------------|-------------------|-------------------|-------|-------------|
| 0.67 gm.----- | 0.01              | 2.67              |       | 1.305       |
| 1.30 gm.----- | 0.00              | 3.25              | 1,242 | 2.895       |
| 4.00 gm.----- | 0.20              | 3.48              |       | 2.625       |

*Example VIII*

Example III was repeated except that six samples were made containing 0.00033 gram, 0.00167 gram, 0.0033 gram, 0.0067 gram, 0.0167 gram, and 0.033 gram of tertiary butylamine borane per mol of silver halide. Sensitometric evaluation provided the following data:

|                | D <sub>min.</sub> | D <sub>max.</sub> | Speed | Total Scale<br>(Log E<br>Range) |
|----------------|-------------------|-------------------|-------|---------------------------------|
| 0.00033 gm.--- | 0.01              | 0.66              | 8,840 |                                 |
| 0.00167 gm.--- | 0.04              | 3.33              | 1,098 | 1.125                           |
| 0.0033 gm.---  | 0.02              | 3.11              | 810   | 1.200                           |
| 0.0067 gm.---  | 0.03              | 2.92              | 550   | 1.305                           |
| 0.0167 gm.---  | 0.09              | 3.56              | 100   | 1.530                           |
| 0.033 gm.---   | 0.13              | 3.24              | 46    | 1.575                           |

*Example IX*

Example VIII was repeated except that the six samples contained the same amounts per mol of silver halide of morpholine borane instead of tertiary butylamine borane. Sensitometric evaluation gave the following data:

|                | D <sub>min.</sub> | D <sub>max.</sub> | Speed | Total Scale |
|----------------|-------------------|-------------------|-------|-------------|
| 0.00033 gm.--- | 0.03              | 1.25              | 6,060 |             |
| 0.00167 gm.--- | 0.04              | 3.36              | 870   | 1.395       |
| 0.0033 gm.---  | 0.05              | 3.07              | 422   | 1.63        |
| 0.0067 gm.---  | 0.07              | 3.53              | 217   | 1.41        |
| 0.0167 gm.---  | 0.10              | 3.42              | 100   | 1.59        |
| 0.033 gm.---   | 0.14              | 3.02              | 46    | 1.575       |

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*Example X*

Example III was repeated except that 0.0167 gram and 0.067 gram of pyridine borane, per mole of silver halide were added to two samples. Sensitometric evaluation provided the following data:

|               | D <sub>min.</sub> | D <sub>max.</sub> | Speed | Total Scale |
|---------------|-------------------|-------------------|-------|-------------|
| 0.0167 gm.--- | 0.03              | 2.28              | 2,616 |             |
| 0.067 gm.---  | 0.04              | 3.32              | 423   | 1.365       |

*Example XI*

Example III was repeated except that no hardener was added and the emulsion was coated on a non-hardening paper support. After exposure the element was developed in a tanning developer to give a wash-off relief when washed with warm water.

Sensitometric evaluation showed a speed of 690 and a reflection D<sub>max.</sub> of 1.00.

*Example XII*

Example III was repeated except that 0.0067 gram of trimethylamine borane and 0.6 gm. of formaldehyde per mole of silver halide were added instead of the trimethyl amine borane alone. Sensitometric evaluations provided the following data:

D<sub>min.</sub> 0.04; D<sub>max.</sub> 4.00; speed, 325; Total scale, 1.335.

*Example XIII*

Example III was repeated except that nine samples were made using the quantities of a mixture of  $\alpha,\beta,\gamma$ -picoline boranes per mole of silver halide as shown in the following table.

Sensitometric evaluation provided the following data:

| Sample No. | Gm. of Borane<br>Comp'd/mole<br>AgHal | D <sub>min.</sub> | D <sub>max.</sub> | Speed | Total Scale |
|------------|---------------------------------------|-------------------|-------------------|-------|-------------|
| 1.-----    | 0.00333                               | 0.00              | 3.00              | 2,112 | 1.395       |
| 2.-----    | 0.00667                               | 0.01              | 3.73              | 680   | 1.125       |
| 3.-----    | 0.013                                 | 0.00              | 3.72              | 490   | 0.960       |
| 4.-----    | 0.0267                                | 0.06              | 3.25              | 530   | 1.020       |
| 5.-----    | 0.04                                  | 0.05              | 3.10              | 407   | 1.125       |
| 6.-----    | 0.0667                                | 0.02              | 3.50              | 107.2 | 1.335       |
| 7.-----    | 0.13                                  | 0.05              | 3.40              | 40.2  | 1.500       |
| 8.-----    | 0.267                                 | 0.15              | 3.40              | 30.2  | 1.305       |
| 9.-----    | 0.4                                   | 0.16              | 3.29              | 44.3  | 1.215       |

The preferred concentrations are 0.013 and 0.0067 gram per mole of silver halide and the speed is 47 to 67 times faster than the control speed of 10.3.

From emulsion coated elements of all the above examples good duplicates can be made by contact printing, using either carbon arc lamps or tungsten photoflood lamps as a light source. The emulsion coated element of Example III is particularly efficacious for reproducing continuous tone negatives, halftones, line copy, engineering drawings, etc. The direct positive elements of this invention may also find use in color photography.

As is evident from the sensitometric data, the photographic elements of this invention provide direct positive images having extremely low minimum densities and high maximum densities and are extremely fast as compared to the direct positive elements of the prior art. The elements of this invention may be developed in any standard developing solution using standard technique. Variations in the developing solution will have much the same effect as it would in developing non-reversal emulsions. No pre-exposure operations or auxiliary processing procedures are necessary or desirable in using the novel elements of this invention. It is also unnecessary to utilize stain producing non-sensitive dyes or other desensitizing compounds in the emulsion. The boranes as chemical fogging agents are far superior to formaldehyde, the prin-

cipal fogging agent of the prior art because the borane compounds do not have any hardening effect on the gelatin layer. This affords a method of providing wash-off relief direct positives by using a hardening developer.

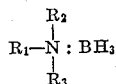
The emulsions of this invention may be coated on any suitable base include paper and transparent film supports. For example, the cellulosic supports, e.g., cellulose acetate, cellulose triacetate, cellulose mixed esters, etc. may be used. Polymerized vinyl compounds, e.g., copolymerized vinyl acetate and vinyl chloride, polystyrene, and polymerized acrylates may also be mentioned. The film can be formed from the polyesterification product of a dicarboxylic acid and a dihydric alcohol made according to the teachings of Alles U.S. Patent 2,779,684 and the patents referred to in the specification of that patent. Other suitable supports are the polyethylene terephthalate/isophthalates of British Patent 766,290 and Canadian Patent 562,672 and those obtainable by condensing terephthalic acid and dimethyl terephthalate with propylene glycol, diethylene glycol, tetramethylene glycol or cyclohexane-1,4-dimethanol (hexahydro-p-xylene alcohol). The films of Bauer et al., U.S. Patent 3,059,543 may also be used. The above polyester films are particularly suitable because of their dimensional stability.

Many borane compounds other than the preferred boranes which are listed above can be used as fogging agents for direct positive photographic elements. Exemplary of such borane compounds would be selected borohydrides. A practical limit is imposed upon the use of certain boranes due to high toxicity and possible explosive characteristics of individual boranes.

What is claimed is:

1. A photographic silver halide emulsion containing an amine borane.

2. A photographic emulsion containing silver halide and an alkyl amine borane of the formula

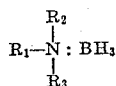


where  $R_1$  is an alkyl radical of 1 to about 20 carbon atoms and  $R_2$  and  $R_3$  are selected from the group consisting of hydrogen and an alkyl radical of 1 to about 20 carbon atoms.

3. A photographic emulsion containing silver halide and a heterocyclic amine borane.

4. A direct positive emulsion containing silver halide and a fogging amount of an amine borane within the range of about 0.00033 to 12 grams of said borane per mole of silver halide.

5. A direct positive emulsion containing silver halide and an alkyl amine borane of the formula



where  $R_1$  is an alkyl radical of 1 to about 20 carbon atoms and  $R_2$  and  $R_3$  are selected from the group consisting of hydrogen and an alkyl radical of 1 to about 20 carbon atoms, said borane being present in a fog producing amount within the range of about 0.00033 to 12 grams per mole of silver halide.

6. A direct positive emulsion as described in claim 5 where said alkyl amine borane is trimethylamine borane.

7. A direct positive emulsion as described in claim 5 where said alkyl amine borane is alamine (tricaprylamine) borane.

8. A direct positive emulsion as described in claim 5 where said alkyl amine borane is dimethyl dodecyl amine borane.

9. A direct positive emulsion as described in claim 5 where said alkyl amine borane is tertiary butylamine borane.

10. A direct positive emulsion containing silver halide and a heterocyclic amine borane, said borane compound being present in a fog producing amount within the range of about 0.00033 to 12 grams per mole of silver halide.

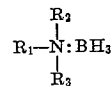
11. A photographic emulsion as described in claim 10 where said heterocyclic amine borane is pyridine borane.

12. A photographic emulsion as described in claim 10 where said heterocyclic amine borane is picoline borane.

13. A photographic emulsion as described in claim 10 where said heterocyclic amine borane is morpholine borane.

14. A photographic element comprising a support and at least one layer having a silver halide emulsion containing an amine borane.

15. A direct positive photographic element comprising a support and at least one layer containing a silver halide emulsion having a fog producing amount of about 0.00033 to 12.0 grams per mole of silver halide of an alkyl amine borane of the formula



where  $R_1$  is an alkyl radical of 1 to about 20 carbon atoms and  $R_2$  and  $R_3$  are selected from the group consisting of hydrogen and an alkyl radical of 1 to about 20 carbon atoms.

16. A photographic element as described in claim 15 where said alkyl amine borane is trimethylamine borane.

17. A photographic element as described in claim 15 where said alkyl amine borane is dimethyl dodecyl amine borane.

18. A direct positive photographic element comprising a support and at least one layer containing a silver halide emulsion having a fog producing amount of 0.00033 to 12.0 grams per mole of silver halide of a heterocyclic amine borane.

19. A direct positive photographic element as described in claim 18 where said heterocyclic amine borane is pyridine borane.

20. A direct positive photographic element as described in claim 18 where said heterocyclic amine is picoline borane.

21. A direct positive photographic element as described in claim 18 where said heterocyclic amine borane is morpholine borane.

22. A direct positive photographic element comprising a film support and at least one layer containing a gelatino-silver chlorobromide emulsion having a fog producing amount of about 0.00033 to 12 grams of an amine borane per mole of said silver chlorobromide.

23. In a process for the preparation of a silver halide photographic emulsion where said emulsion is ripened, washed and digested the improvement which comprises adding a fog producing amount of about 0.00033 to 12 grams per mole of said silver halide of an amine borane subsequent to the washing of said emulsion.

24. A process as defined in claim 23 where said amine borane is added in a fog producing amount of about 0.013 to 1.3 grams per mole of said silver halide.

#### References Cited

#### UNITED STATES PATENTS

3,246,987 4/1966 Hanson et al. 96-59

70 NORMAN G. TORCHIN, Primary Examiner.

R. E. FICHTER, Assistant Examiner.